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# Plastics — Thermogravimetry (TG) of polymers —

## Part 2:
## Determination of activation energy

*Plastiques — Thermogravimétrie (TG) des polymères —*

*Partie 2: Détermination de l'énergie d'activation*

Reference number
ISO 11358-2:2005(E)

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# Foreword

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ISO 11358-2 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

# Plastics — Thermogravimetry (TG) of polymers —

## Part 2:
## Determination of activation energy

## 1   Scope

This part of ISO 11358 specifies a method for the determination of the activation energy, $E_a$, in the Arrhenius equation for the decomposition of polymers using a thermogravimetric technique. The method is applicable only if the reaction proceeds by a single mechanism. It is applicable to multistage reactions if they consist of clearly separated single-stage steps.

NOTE        The term activation energy is more suited to describing the kinetics of gas-phase reactions. When chemical reactions start from the solid state as in this part of ISO 11358, this parameter is nevertheless used for practical purposes.

## 2   Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11358:1997, *Plastics — Thermogravimetry (TG) of polymers — General principles*

## 3   Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11358 and the following apply.

**3.1**
**Arrhenius equation**
equation representing the temperature dependence of the rate constant of a reaction

NOTE        The rate constant, $k$, of a reaction is expressed by the Arrhenius equation, as follows:

$$k = A \exp^{(-E_a/RT)} \tag{1}$$

where

$R$     is the gas constant (= 8,314 $J \cdot K^{-1} \cdot mol^{-1}$);

$T$     is the absolute temperature, in kelvins (K);

$A$     is the pre-exponential factor, in reciprocal seconds ($s^{-1}$);

$E_a$     is the activation energy, in $J \cdot mol^{-1}$;

$k$     is the rate of reaction (= $d\alpha / dt$), in reciprocal seconds ($s^{-1}$).

**3.2**
**activation energy**
$E_a$
energy, above that of the ground state, which must be added to an atomic or a molecular system to allow a particular process to take place

NOTE    It is expressed in $J \cdot mol^{-1}$.

**3.3**
**degree of conversion**
$\alpha$
quantity of products present at a particular time and temperature during a reaction compared with the final quantity of the products

NOTE 1    It is given by the equation:

$$\alpha = (M_i - M_t) / (M_i - M_f) \tag{2}$$

where

$M_i$    is the initial quantity, in mg;

$M_t$    is the quantity at a particular time and temperature, in mg;

$M_f$    in the final quantity, in mg.

NOTE 2    When multistage reactions occur, the degree of conversion is calculated separately for each stage.

NOTE 3    The degree of conversion is dimensionless and varies in value from 0 to 1.

# 4    Principle

Test specimens are heated at several different heating rates and the change in mass measured as a function of temperature. The temperatures corresponding to given degrees of conversion are determined for each heating rate. For a given degree of conversion, the logarithm of the heating rate is plotted against the reciprocal of the absolute temperature, and the activation energy is calculated from the slope of straight line thus obtained.

# 5    Apparatus

See ISO 11358:1997, Clause 5.

# 6    Mass and temperature calibration

## 6.1    Mass calibration

See ISO 11358:1997, Subclause 7.1.

## 6.2    Temperature calibration

See ISO 11358:1997, Subclause 7.2.

## 7   Test specimens

The test specimens shall be in the form of powder, pellets, flakes, filaments or film. The test specimens shall be prepared by cutting the material, as necessary, to a size appropriate for the apparatus (see ISO 11358:1997, 6.1). Particles of small size, i.e. of high surface area to volume ratio, are preferred. Grinding in a liquid-nitrogen mill may be used to decrease the particle size.

## 8   Procedure

### 8.1   General

See ISO 11358:1997, Clause 8

Perform the procedure at three or more heating rates, using specimens of identical mass ($\pm 1$ %). The lowest and highest heating rates shall differ by a factor of at least 5.

In order to improve the accuracy of the determination, record the mass of an empty pan subjected to the same test conditions of atmosphere, gas flow and heating rate as used in the run with the specimen. If there is a mass change during the run with the empty pan (which is usually ascribed to buoyancy), subtract the curve obtained with the empty pan from that obtained with the test specimen to obtain a corrected thermogravimetric curve for the specimen. This procedure shall be repeated for all heating rates. Corrected curves shall be used for the analysis of the results.

NOTE      It is preferable to use specimens less than 10 mg in size and heating rates of less than 10 K·min$^{-1}$. For specimens greater than 10 mg and heating rates greater than 10 K·min$^{-1}$, the specimen temperature may not follow the required temperature profile.

### 8.2   Non-oxidative reactions

When required, an inert-gas atmosphere (e.g. nitrogen) shall be maintained during the determination to prevent oxidation of the specimen. Only purified gas (purity at least 99,95 %) shall be used to create the inert atmosphere.

### 8.3   Oxidative reactions

An oxidative gas atmosphere (oxygen or air) shall be used when testing polymers that undergo oxidation reactions. Details of the type and purity of the gas used shall be included in the test report.

## 9   Expression of results

### 9.1   Graphical presentation

Present the thermogravimetry data obtained in the form of a mass change or percentage mass change versus temperature curve. Determine specific temperatures from the TG curve using the procedures described in ISO 11358:1997, Clause 9

### 9.2   Determination of energy of activation

Check that the final mass reached at the end of each measurement run is constant, thereby indicating completion of the reaction, and that the percentage change in mass from the start of the run to the end of the run for each of the heating rates is also the same.

For a given degree of conversion, $\alpha$, determine, from the TG curves, the absolute temperatures for each of the heating rates, $\beta$. Repeat for other degrees of conversion. Typical curves are shown in Figure 1.
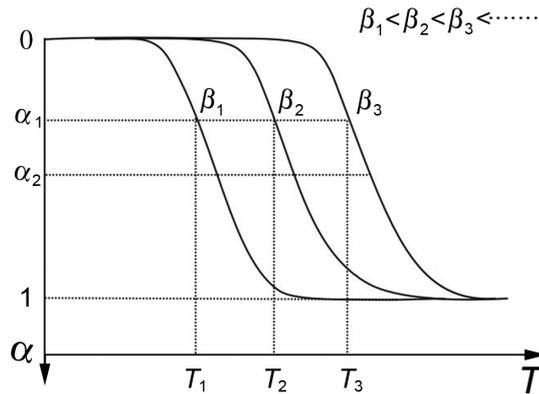
**Figure 1 — Determination of absolute temperature for a given degree of conversion and heating rate**

The approximate relationship given by Equation (3) was derived by Ozawa and later by Flynn and Wall (see References [1] and [2] in the Bibliography) and is used to determine the activation energy, $E_a$.

$$\log\beta + 0{,}456\ 7(E_a/RT) = \text{constant} \tag{3}$$

where $E_a$ and $R$ are the activation energy and the gas constant ($R = 8{,}314\ \text{J·K}^{-1}\text{·mol}^{-1}$), respectively.

For heating rates $\beta_1$, $\beta_2$, $\beta_3$, …, and temperatures $T_1$, $T_2$, $T_3$, …, Equation (4) is obtained for a given degree of conversion, $\alpha_1$:

$$\log\beta_1 + 0{,}456\ 7(E_a/RT_1) = \log\beta_2 + 0{,}456\ 7(E_a/RT_2) = \log\beta_3 + 0{,}456\ 7(E_a/RT_3) \tag{4}$$

Plotting the logarithm of the heating rate, $\log\beta$, against the reciprocal of the absolute temperature, $T^{-1}$, for each degree of conversion $\alpha$ gives a series of straight-line curves (see Figure 2), and the activation energy, $E_a$, is calculated from the slope ($-0{,}456\ 7E_a/R$) in each case.

NOTE 1    This method is not suitable for very high degrees of conversion.

NOTE 2    This method is not reliable when the value of $E_a$ varies widely from one degree of conversion to another and/or the $\log\beta$ vs. $T^{-1}$ relationship is not linear.
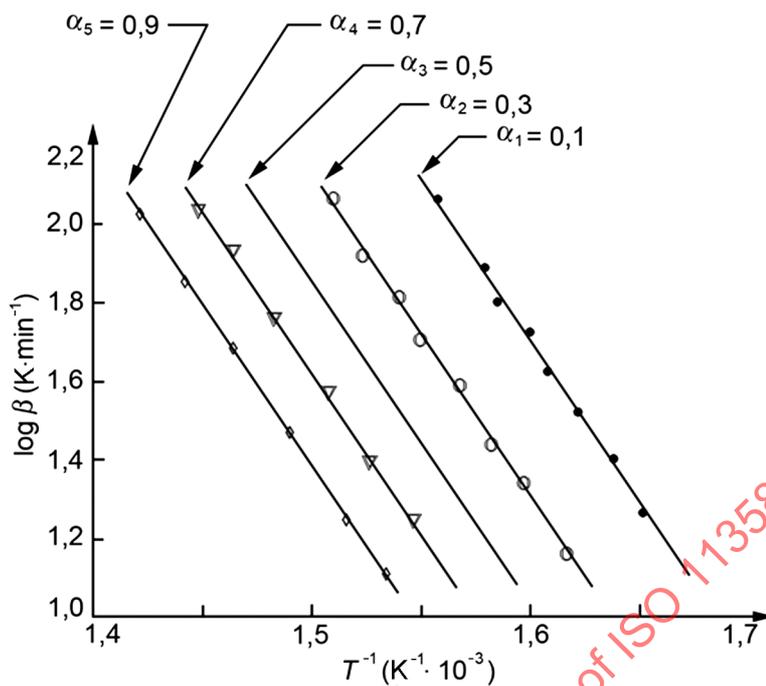
**Figure 2 — Heating rate versus the reciprocal of the absolute temperature**

## 10 Precision

See Reference [3] in the Bibliography.

## 11 Test report

The test report shall include the following information:

a) a reference to this part of ISO 11358;

b) all details necessary for complete identification of the material analysed;

c) the form and dimensions (if applicable) of the test specimen;

d) the mass of the test specimen;

e) details of the conditioning of the specimen prior to the test;

f) the specimen pan size and material of construction;

g) the atmosphere and gas-flow rate used;

h) the heating rates used.

i) the standard reference material used for temperature calibration;

j) the activation energy determined using Equation (1) or (3);

k) any observations regarding equipment, test conditions or test specimen behaviour;

l) the date of the determination.